SOLUBILITY OF SULFUR IN SHERGOTTITIC SILICATE MELTS UP TO 0.8 GPA: IMPLICATIONS FOR S CONTENTS OF SHERGOTTITES.

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Introduction: Shergottites have high S contents (1300 to 4600 ppm; [1]), but it is unclear if they are sulfide saturated or under-saturated. This issue has fundamental implications for determining the long term S budget of the martian surface and atmosphere (from mantle degassing), as well as evolution of the highly siderophile elements (HSE) Au, Pd, Pt, Re, Rh, Ru, Ir, and Os, since concentrations of the latter are controlled by sulfide stability. Resolution of sulfide saturation depends upon temperature, pressure, oxygen fugacity (and FeO), and magma composition [2]. Expressions derived from experimental studies allow prediction of S contents, though so far they are not calibrated for shergottitic liquids [3-5]. We have carried out new experiments designed to test current S saturation models, and then show that existing calibrations are not suitable for high FeO and low Al_2O_3 compositions characteristic of shergottitic liquids. The new results show that existing models under-predict S contents of sulfide saturated sherottitic liquids by a factor of 2.

Experiments: Two shergottite compositions – one evolved (modelled after EET A79001 lithology B; [1]) and a second more primitive (modelled after Yamato 980459; [1]) - are currently being studied so that effects of melt compositional variation on sulfide saturation can be evaluated. Experiments at 1 bar consisted of mixtures of evolved shergottitic bulk compositions and FeS in alumina capsules (with an oxygen buffer in a separate alumina capsule) sealed into silica tubes and equilibrated in Deltech furnaces for 48-72 hrs [6]. For experiments at 0.8 GPa, two types of capsules were used: graphite and MgO. Runs were conducted at a constant pressure (0.8 GPa) using a piston cylinder apparatus. Once the samples were under pressure, they were heated to silicate superliquidus temperatures and allowed to equilibrate for a set amount of time depending on the run temperature. A Type C thermocouple (W-Re) wire with an accuracy of ±2° C was used to measure temperature. Oxygen fugacity of the experiments was FMQ-2 for the graphite capsule experiments (see also [7]), and slightly lower for the MgO capsule experiments. The amount of Fe_2O_3 in the glass in either capsule type is small, < 5%. The samples were then quenched to glass containing large sulfide liquid spheres.
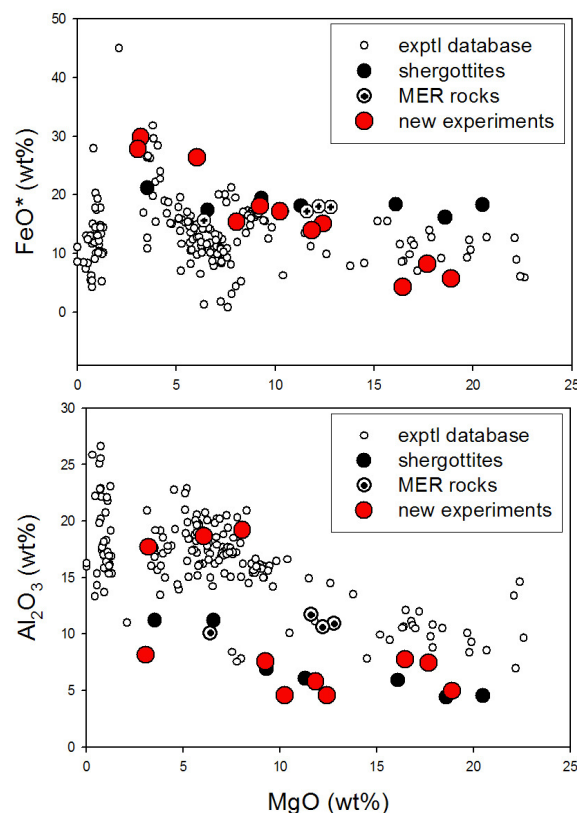

Figure 1: Compositions of silicate melts in new experiments (red) compared to shergottite meteorites (solid black), MER compositions (circles with dots), and the experimental database (from [3]) used to calibrate sulfide salturation models. The new experiments have glass FeO and Al_2O_3 contents that are closer to those of shergottites and MER.

The two different series (MgO and C capsules) were carried out at 0.8 GPa and temperatures between 1450° and 1300° C (Table 1).

Analysis: Samples were analyzed for major elements in the glass (including S) using the electron microprobe at NASA-JSC. Operating conditions were accelerating voltage of 20 kV and sample current of 20 nA [6].

Calculations: The S content of a silicate melt in equilibrium with sulfide liquid is known to be a function of T, P, fO_2, and bulk composition [2]. Recent calibrations have included the effects of all of these variables. We consider several recent models [3-5]

for predicting S contents in silicate melts, and choose the model of [3] due to the similarity in compositions used in the experimental database upon which it is calibrated. We then use this model to compare predicted S contents to those measured in our experimental shergottitic glasses. Comparison of 1 bar, Al_2O_3-rich melt compositions are in good agreement with model predictions. This may be due to the fact that these melts are similar in composition to many melts used to calibrate the saturation models. However, melts with lower Al_2O_3 and high FeO, like shergottite compositions, contain much higher S contents than predicted by existing models. The most dramatic example is from experiment #16 at 0.8 GPa and 1350 ℃, which is predicted to contain 1600 ppm S, but contains 3200 ppm (Fig. 2). More experiments are underway to explore melt compositional ranges in Al_2O_3, FeO and MgO covering the entire range for shergottites.

Implications: Because shergottite parent melts are likely generated at higher pressures [8,9], and sulfide saturation has a negative pressure dependence, melts from the martian mantle may initially be saturated in the source region, become under-saturated during ascent, and then become saturated again upon subsequent differentiation in the crust. Preliminary assessments indicate that most shergottites may be sulfide under-saturated, whereas a few (Dho 019 and EET A79001 lithology B) appear to be sulfide saturated, since they have S contents as high as those predicted at saturation. The two groups also have distinctly different HSE concentrations [10,11], showing that sulfide saturated shergottites contain much lower HSE contents than sulfide undersaturated shergottites.
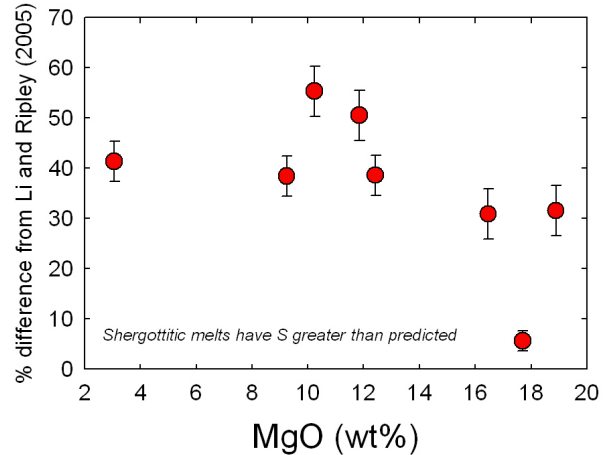

Figure 2: Percent difference between measured and predicted S contents of experimental shergottitic melts, plotted versus MgO contet of the melt. Predicted values are using model of Li and Ripley (2005). Differences may be systematically greater for more evolved, low MgO melts.

References: [1] Meyer, C. Jr., (2008) website: http://curator.jsc.nasa.gov/antmet/mmc/index.cfm; [2] Wallace, P.J. and Carmichael, I.S.E. (1992) *GCA* 56: 1863-1874; [3] Li, C. and Ripley, E.M. (2005) *Mineralium Deposita* 40: 218-230; [4] Liu, Y. et al. (2007) *GCA* 71: 1783-1799; [5] Holzheid, A. and Grove, T.L. (2002) *Amer. Mineral.* 87: 227-237; [6] Righter, K. et al. (2006) *Chem. Geol.* 227: 1-25; [7] Medard et al. (2008) *Amer. Mineral.* 93, 1838-1844; [8] Monders, A.G. (2007) *MAPS* 42, 131-148; [9] Musselwhite, D.S. et al. 2006. *MAPS* 41: 1271-1290; [10] Puchtel, I. et al. 2008. *Lunar Planet Sci.* XXXIX, #1650; [11] Jones, J.H. et al. 2003. *Chem. Geol.* 196:21-41.

Table 1: Summary of experimental and analytical results; all experiments at 0.8 GPa

Run	T (°C)	Dur. (hr)	Capsule	MgO (wt%)	FeO (wt%)	Al_2O_3 (wt%)	S (ppm) measured	S (ppm) [3]	% diff.
8	1350	5	MgO	16.46	4.27	7.76	2300	1590	31
7	1400	4	MgO	18.89	5.74	4.96	2600	1780	32
4	1450	2	MgO	17.69	8.23	7.42	2400	2270	6
21	1300	2	C	9.24	18.07	7.58	3200	2000	38
20	1300	6	C	3.06	27.77	8.14	5600	3280	41
16	1350	5	C	11.84	13.99	5.78	3200	1600	51
13	1400	4	C	12.42	15.09	4.57	3300	2050	39
6	1450	2	C	10.24	17.17	4.57	5200	2300	55